THE ULTRAVIOLET ABSORPTION SPECTRA OF SOME ORGANIC COMPOUNDS

BY

BARBARA WILLIAMSON

B.A., Texas State College for Women, 1938

AN ABSTRACT OF A THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN
CHEMISTRY IN THE GRADUATE SCHOOL OF
THE UNIVERSITY OF ILLINOIS, 1941

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Theoretical

Just as the valence electrons of the atom are responsible for its chemical properties, so the same bonding electrons in the molecule give rise to the ultraviolet absorption spectrum. When the constituent atoms are exerting their maximum valence, the single bonds thus formed are of such high energy that the compound's absorption occurs in the far ultraviolet. On the other hand, the so-called double bond is essentially weaker in character. Therefore, unsaturated compounds such as those studied in this thesis will absorb light at longer wavelengths, namely, the visible and near ultraviolet regions.

The relative weakness of the double bond lies in its composite nature. Taking the most common case as an example, the four valence electrons of carbon are disposed in the following manner: Three of the carbon's bonds lie in the plane of the atoms. It is generally conceded that the electron bonding the other carbon of the double bond is largely of s-character, while the two singly bonding electrons are of the σ-type. (The σ-bonding is the well-known hybrid s-p orbital (1:3) resulting in maximum bond energy.[1]) The second part of the double bonding, however, consists in the interaction of two electrons in the so-called π state, which interaction occurs in a plane perpendicular to the plane of the atoms. For carbon the π electrons would have the typical dumb-bell configuration of p_z electrons.

Now the unique properties of the double bond may be attributed to the interaction between the lobes, lying above and below the plane of the atoms, of such π electrons. Two conclusions may be drawn from this concept. First, the longer a conjugated chain, the greater the overall interaction between the π electrons from one end to the other. Secondly,

maximum interaction between the π electrons will occur for a *coplanar configuration.* Both these conditions will be evidenced by the absorption curve of a conjugated system. The longer the conjugated chain, the longer the wavelength at which the compound absorbs. If the conjugated chain is effectively "broken" by being twisted from coplanarity at some point, then the chain is divided into two smaller conjugated systems, which halves interact only slightly.

Experimentally, the non-coplanarity may be accomplished by steric hindrance. The effect was first reported, though not recognized, by Ley and Rinke[2] when they observed that substitution of a methyl group or groups on the alpha carbons of trans-stilbene reduced the absorption and shifted the curve toward the violet. Hindered biphenyls showing decreased absorption due to restricted rotation have been investigated in this thesis as a continuation of the work of O'Shaughnessy and Rodebush.[3] Substituted stilbenes and related compounds were also studied. In both type cases the greater the steric hindrance between substituent groups, the more the system is twisted out of coplanarity. Decreased absorption and shifting toward shorter wavelengths gives evidence that the overall conjugation typical of the biphenyl or stilbene system has been broken.

Experimental

The apparatus used was a Bausch and Lomb medium quartz spectrograph fitted with a rotating sector. A condensed spark between tungsten steel electrodes was the light source. The fused quartz absorption cells were 5.0000 ± 0.0001 cm. long and were optically matched.

An adaption of the Henri method[4] was followed. Duplicate samples were weighed out by the microanalyst to five significant figures. Dilutions of approximately 0.001, 0.0001, and 0.00001 mols/liter were then made. Occasionally it was necessary to use additional concentrations to cover all features of the absorpti on curve. One set of solutions was run

immediately; the other set was allowed to stand a week and then run. This served the double purpose of (a) insuring against any progressive reaction of the compound with the solvent and (b) checking the absorption curve.

The solvent used was either n-hexane or 95% ethyl alcohol, preferably the former. The n-hexane was purified according to the procedure outlined in O'Shaughnessy and Rodebush.[3]

The plates were read visually. This involved the largest error of the procedure, three to five percent.

(The work on the substituted stilbenes and related compounds was largely exploratory in nature, the compounds were occasionally of doubtful structure and consequently only moderate accuracy was observed in this part of the research.)

Data obtained are as follows:

No.	Compound	Solvent	$\lambda_{max.}$	$\epsilon_{max.}$
1.	2,2′-dimethoxy biphenyl	n-hexane	2767 A.	6,000
2.	4,4′-dimethoxy biphenyl	n-hexane	2630	21,700
3.	2,2′-dihydroxy biphenyl	alcohol	2420 2850	10,000 6,000
4.	3,3′-dihydroxy biphenyl	alcohol	2550	12,000
5.	4,4′-dihydroxy biphenyl	alcohol	2650	22,400
6.	2,2′-dicarboxy biphenyl	alcohol	2800	2,200
7.	3,3′-dicarboxy biphenyl	alcohol	ϵ = 20,000 at 2430	
8.	4,4′-dicarboxy biphenyl (dimethyl ester)	alcohol	2800	30,000
9.	2.2′-diamino biphenyl	alcohol	2920	5,000
10.	4,4′-diamino biphenyl	alcohol	2850	23,200
11.	2,2′-dinitro biphenyl	alcohol	2570	12,000
12.	3,3′-dinitro biphenyl	alcohol	3373	18,000
13.	4,4′-dinitro biphenyl	alcohol	3050	24,000
14.	Diphenyl 2,2′-disulfonic acid (disodium salt)	alcohol	2777	2,000
15.	2,2′-dichloro biphenyl	alcohol	ϵ = 4,500 at 2350, falls steadily	
16.	4,4′-dichloro biphenyl	alcohol	2600	21,700
17.	4,4′-difluoro biphenyl	alcohol	2430	17,000
18.	4,4′-dibromo biphenyl	alcohol	2620	23,300
19.	4,4′-diiodo biphenyl	alcohol	2740	30,000
20.	Mesitaldehyde	n-hexane	2610	12,000

21. 2,4-dimethyl-3-chloro-6-methoxy acetophenone	n-hexane	$\epsilon_{min.}$ = 500 at 2650	
22. 1,2-dimesityl ethylene (trans)	n-hexane	2630	18,000
23. 2,3-dimesityl butene-2	n-hexane	ϵ = 8,000 at 2350, falls steadily	
24. 1,2-dimesityl vinyl alcohol	n-hexane	2550	18,000
25. 1,2-dimesityl-1-propen-1-ol	n-hexane	ϵ = 8,000 at 2350, falls steadily	
26. 1,2-diduryl acetylene glycol (cis)	n-hexane	ϵ = 3,500 at 2350, falls steadily	
27. 1,2-diduryl acetylene glycol (trans)	n-hexane	ϵ = 3,500 at 2350, falls steadily	
28. 2,3-dimesityl butane	n-hexane	ϵ = 11,000 at 2350, falls steadily	
29. Desoxymesitoin	n-hexane	ϵ = 8,000 at 2350, falls steadily	
30. Mesitil	n-hexane	ϵ = 6,500 at 2350, falls steadily	
31. Mesityl phenyl diketone	n-hexane	2640	14,000
32. 2,3-dimesityl butadiene-1,3	n-hexane	ϵ = 10,000 at 2400, falls steadily	
33. α-mesityl vinyl mesityl ketone	n-hexane	ϵ = 7,000 at 2350 falls steadily	
34. 2,3-diphenyl butadiene-1,3	n-hexane	2350	18,000
35. 1-phenyl-1-mesityl ethylene	n-hexane	2560	12,000

Discussion of Results

(1). The ortho, ortho′ biphenyls demonstrate further evidence for O'Shaughnessy and Rodebush's ideas of restricted rotation. In addition, it appears that the nature of the substituents, i.e. whether auxochromic (ortho-para directing) or antiauxochromic (meta directing), influences the absorption curve. In certain cases the spatial configuration of the group

may also have some effect.

A biphenyl disubstituted in the ortho positions will show a complete lack of a biphenyl peak. (The exception to this is 2,2′-dihydroxy biphenyl where the hydroxyl groups are sufficiently small to allow some rotation and consequently the compound exhibits a diminished biphenyl peak.) In addition, the compound will show an absorption characteristic of the benzene ring plus substituent. This is because the resonance across the link between the two biphenyl rings has been broken to such an extent as to effectively produce two benzene nuclei.

Now if the biphenyl is substituted with auxochromic substituents, the two biphenyl halves will absorb *more* than two separate benzene nuclei, i.e. $\epsilon_{max.}$ (biphenyl) $>$ $\epsilon_{max.}$ (2 x benzene). Since it is the ionic form of the molecule which is actually responsible for light absorption, one possible hypothesis is that auxochromic substituents in the ortho positions, being ortho-para directing, will be activated by the biphenyl link. The opposite behavior would be expected for anti-auxochromic substituents. Thus the biphenyl resonance across the rings either enhances or detracts from the ionic forms of the benzene halves thus making an ortho, ortho′ biphenyl substituted with auxochromes absorb more effectively that two benzene nuclei and vice versa. This idea is borne out by the absorption curves with the exception of diphenyl 2,2′-disulfonic acid (disodium salt).

The spatial configuration requirements for 2,2′-dinitro and 2,2′-dicarboxy biphenyl would tend to further cut the absorption below that of twice the benzene derivative. When, in order to resonate with the ring, these more or less flat, triangular groups are in a coplanar position with the parent benzene ring, they are also in the least favorable position, sterically.

(2). For the meta, meta′ biphenyls a marked difference is observed between the absorption curves of a compound substituted with auxochromic substituents and one substituted with antiauxochromic substituents. In contrast to the

corresponding ortho, ortho′ biphenyls, resonance across the link between the rings would tend to enhance the ionic forms of the antiauxochromic biphenyls, evidenced by an abrupt rise at short wavelengths, but decrease the absorption for meta, meta′ biphenyls with auxochromic substituents, resulting in a decreased biphenyl peak plus benzene absorption.

(3). The para, para′ biphenyls show no new effects. It is possible that the absorption spectra for these compounds may be taken as a measure of the electromeric amphoterism of a functional group, i.e. the ease with which it may either accept or donate electrons from or to the benzene ring.

(4). It has been shown that the absorption curve is a good criterion for distinguishing between linear and crossed conjugated systems provided they are not too heavily substituted. In this work, it was found that the system $\phi\text{-}\underset{|}{\overset{|}{C}}\!=\!\underset{|}{\overset{|}{C}}\text{-}\phi$ absorbed at longer wavelengths and larger extinction coefficients than the corresponding crossed system $\phi\text{-}\underset{\|}{\overset{|}{C}}\text{-}\phi$.

$$\overset{\|}{C}$$

In case of heavy substitution it is conclusively demonstrated that steric hindrance twists the system, linear or crossed, completely out of coplanarity.

(5). Confirmation of the rapidity of oxidation of a cis ene-diol compared to the trans form may be shown from absorption data.

(6). Further evidence of increasing steric hindrance with increasingly large alkyl substituents in the mesityl alkyl ketones is cited. (This work was done in collaboration with O'Shaughnessy.)

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VITA

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